Hydrido(triaryl phosphite) Complexes of Cobalt, Rhodium, and Iridium

By J. J. LEVISON and S. D. ROBINSON*

(*Department of Chemistry, King's College, Strand, London, W.C.2*)

TERTIARY organo-phosphites are rapidly gaining recognition as versatile and important ligands for the Group VIII metals. Recent interest[1] in hydrido(trialkyl phosphite) complexes of cobalt and iron prompts this report of related hydrido-(triaryl phosphite) complexes of cobalt, rhodium, and iridium.

Reduction of cobalt(II) salts by ethanolic sodium borohydride solution at 25° in the presence of excess of triaryl phosphite leads to rapid formation of the hydrido-complexes $CoH[P(OAr)_3]_4$ in good yield. The complexes recrystallise from benzene as pale yellow, hexagonal platelets, m.p. *ca.* 160°, soluble in non-polar solvents and stable to air for several weeks. The known tetrakis(triaryl phosphite)nickel(0) complexes may be prepared by a similar method. The i.r. spectra of the cobalt and nickel complexes are almost identical, in particular, the cobalt derivatives show no clearly defined bands in the range 1600—2500 cm.$^{-1}$ attributable to Co–H stretching vibrations. However the hydrido formulation for the cobalt complexes is confirmed by the presence in the n.m.r. spectra of a quintet at high field with intensity ratios 1 : 4 : 6 : 4 : 1 (J_{PH} *ca.* 17 c./sec.). Some line broadening attributable to coupling with the cobalt quadrupole is also observed. Similar results for the complex $CoH[P(OEt)_3]_4$ have been interpreted in terms of a square pyramidal (C_{4v}) structure.[1] However *X*-ray powder photographs indicate that the compounds $CoH[P(OPh)_3]_4$ and $Ni[P(OPh)_3]_4$ are isomorphous; this suggests a tetrahedral configuration for the four phosphite ligands in the cobalt complex, probably with the hydride ligand situated along a trigonal axis as postulated[2] for $CoH(Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2)_2$. The apparent magnetic equivalence of the ^{31}P nuclei may be a characteristic of this particular rigid stereochemistry or may indicate a rapid intramolecular ligand rearrangement in solution. The chemical stability of these cobalt hydrides is remarkably high in comparison with most other cobalt(I) hydrides; however similar stability has been reported[3] for the closely related complex $CoH(PF_3)_4$.

The hydridotetrakis(triaryl phosphite)rhodium complexes $RhH[P(OAr)_3]_4$ may be prepared as white crystalline solids by reaction of $RhH(CO)(PPh_3)_3$ with an excess of triaryl phosphite under mild conditions (ethanol under reflux, 2—3 min.). These rhodium complexes show no bands in the i.r. spectrum attributable to Rh–H stretching vibrations but may be characterised as hydrido-complexes by their high field n.m.r. spectra which contain a 1 : 4 : 6 : 4 : 1 quintet pattern (J_{PH} *ca.* 45 c./sec.). Each member of the quintet is further split into a sharp doublet by coupling with ^{103}Rh (J_{RhH} *ca.* 8 c./sec.). This pattern is consistent with a structure similar to that discussed for the cobalt analogues. The high field n.m.r. spectra of $RhH(PPh_3)_4$ show line broadening and loss of fine structure attributable[4] to rapid ligand exchange while the sharp well-resolved spectra of the complexes $RhH[P(OAr)_3]_4$ indicate that ligand exchange is absent or too slow to cause line broadening. This observation is in accord[4] with the high π-acidity of the $P(OAr)_3$ ligands relative to PPh_3.

Attempts to isolate similar iridium(I) hydrido-complexes from the solutions formed by reaction of $IrH(CO)(PPh_3)_3$ with triaryl phosphites in ethanol have failed. However, i.r. and high-field n.m.r. spectral studies on reaction solutions in benzene clearly show formation of the complexes $IrH(CO)[P(OAr)_3]_3$ with trigonal bipyramidal (C_{3v}) structures ($\nu_{C=O}$ 1980 cm.$^{-1}$; τ *ca.* 21, quartet, J_{PH} 14 c./sec.) as the major products under mild conditions.

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[1] R. D. Mullineaux, U.S.P. 3,290,348 (*Chem. Abs.*, 1967, **66**, 65,080); W. Kruse and R. H. Atalla, *Chem. Comm.*, 1968, 921.

[2] A. Sacco and R. Ugo, *J. Chem. Soc.*, 1964, 3274.

[3] T. Kruck, *Angew. Chem. Internat. Edn.*, 1967, **6**, 53, and references therein.

[4] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.